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THE VISCOSITY AND THERMAL CONDUCTIVITY COEFFICIENTS OF DILUTE NITROGEN AND OXYGEN

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THE VISCOSITY AND THERMAL CONDUCTIVITY COEFFICIENTS OF DILUTE NITROGEN AND OXYGEN

G. E. Childs and H. J. M. Hanley

The coefficients of viscosity and thermal conductivity for dilute nitrogen and oxygen were examined using a method proved suitable for argon. Given the kinetic theory expressions for the transport coefficients, this method indicates a selection of a potential function and its parameters to correlate theory with experimental data. The potential functions chosen were the Lennard-Jones, Kihara, Exp: 6, and the Morse. It was found that the Kihara was most suitable and theoretical viscosity coefficients were computed with this function. The usual correction to the kinetic theory equation for thermal conductivity, the Eucken correction, was found not to be sufficient and it was decided to use an empirical polynomial equation to correlate the thermal conductivity coefficients. Tables of the transport coefficients for both gases are given between 100 and 1000°K.

Key Words: Dilute gases, Nitrogen, Oxygen, Transport coefficients, Lennard-Jones, Kihara, Exp: 6, Morse potential functions, Eucken correction, Correlation.

1. INTRODUCTION

The viscosity and thermal conductivity coefficients of dilute nitrogen and oxygen can be calculated from the Chapman-Enskog kinetic theory expressions [1] *. As these expressions are known to be satisfactory, the problem, as for all dilute gases, is that of choosing a suitable potential function and the best force constants for that function. The method of selection used here is the same as that proved successful for dilute argon [2, 3]. The kinetic theory thermal conductivity equation is not applicable for polyatomic gases and the usual procedure is to apply the Eucken correction [1]. However, it was found that this did not give satisfactory results and it was necessary to use a polynomial expression.

*Numbers in brackets refer to references.

2. THE POTENTIAL FUNCTIONS

The discussion was restricted to the four most commonly used functions: the Lennard-Jones, the Kihara, the Exp: 6, and the Morse. The Kihara, in particular, has received much attention in the literature recently [4, 5, 6]. The Morse function has also been described by several authors [7, 8]. As the functions are well known and have been fully discussed, it is necessary only to outline them here. If $U(r)$ is the interaction potential of two molecules separated by distance r , and ϵ is the maximum energy of attraction, or energy minimum, the potentials are written:

Lennard-Jones

$$U(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] , \quad (1)$$

where σ is the value of r at $U(r) = 0$.

Kihara

$$U(r) = \left[\left(\frac{\sigma - a}{r - a} \right)^{12} - \left(\frac{\sigma - a}{r - a} \right)^6 \right] , \quad r > a \quad (2)$$

$$U(r) = \infty , \quad r \leq a.$$

Here the finite size of the molecule is taken into consideration by including a core diameter, a . (For the Lennard-Jones, $a=0$.) A reduced parameter γ is defined as a/σ .

Exp: 6

$$U(r) = \frac{\epsilon}{1-6/\alpha} \left[\frac{6}{\alpha} e^{\alpha(1-r/r_m)} - (r_m/r)^6 \right] , \quad (3)$$

where r_m is the value of r at the energy minimum and α a parameter which represents the steepness of the repulsive part of the function.

Morse

$$U(r) = \epsilon \left\{ \exp \left[-2 \left(\frac{c}{\sigma} \right) (r - r_m) \right] - 2 \exp \left[- \left(\frac{c}{\sigma} \right) (r - r_m) \right] \right\}, \quad (4)$$

where c is related to the curvature of the potential at $r = r_m$.

3. KINETIC THEORY EXPRESSIONS FOR THE VISCOSITY AND THERMAL CONDUCTIVITY COEFFICIENTS

The kinetic theory for a dilute gas is formally complete [1]; the Chapman-Enskog treatment of the Boltzmann equation gives the viscosity and thermal conductivity coefficients in terms of collision integrals which are functions of the gas dynamics and thus of the intermolecular potential. It is the lack of knowledge of the latter which restricts the applicability of the kinetic theory expressions. These expressions are:

Viscosity (η)

$$\eta 10^7 = \frac{266.93 (MT)^{1/2}}{R^2 \Omega^{(2,2)*}(T^*)} f_{\eta} \text{ g cm}^{-1} \text{ sec}^{-1}, \quad (5)$$

Thermal Conductivity (λ)

$$\lambda 10^7 = \frac{8322.4 (T/M)^{1/2}}{R^2 \Omega^{(2,2)*}(T^*)} f_{\lambda} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}, \quad (6)$$

where: M = molecular weight. ($M = 28.0134$ for nitrogen
 $M = 31.9988$ for oxygen)

R = a distance parameter, i.e., $R \equiv \sigma$ for the
Lennard-Jones, Kihara, and Morse; and $R \equiv r_m$
for the Exp: 6.

T = the absolute temperature, °K.

$\Omega^{(2,2)*}(T^*)$ = the reduced collision integrals
(reduced by dividing by the integrals for the
rigid sphere case) at the reduced temperature
 T^* , where $T^* = T/(\epsilon/k)$ with k the Boltzmann
constant.

The terms f_η and f_λ account for higher mathematical approximations to η and λ and are slowly varying functions of T^* which seldom differ from unity by more than about 0.5%. To be consistent with the accuracy of the experimental viscosity and thermal conductivity data at extreme temperatures, they can be omitted from Eqs (5) and (6) without significant error.

Tables of the collision integrals as a function of T^* for each of the potentials were taken from Refs. 1, 6, 7, and 9. The numerical values of the integrals depend on the method of integration, but it was verified that the choice of any particular set of tables made no significant difference to the results presented here.

For polyatomic gases the Eucken correction modifies Eq (6) to:

$$\lambda_{\text{Eucken}} = \lambda_{\text{dilute}} \left(\frac{4}{15} \frac{C_v}{R} + \frac{3}{5} \right), \quad (7)$$

where λ_{dilute} is the Chapman-Enskog value (Eq (6)), C_v is the specific heat of the gas at constant volume and R the gas constant. The Eucken factor contributes 0.25% at low temperature and 0.4% at high temperature to the total conductivity.

4. EXPERIMENTAL DATA

The experimental data were taken from the following references:

Nitrogen, viscosity, Refs. 10-25

temperature range 75 - 1200 °K.

Oxygen, viscosity, Refs. 10, 12-17, 21, 23, 26-29

temperature range 75 - 1166 °K.

Nitrogen, thermal conductivity, Refs. 30-48

temperature range 75 - 1173°K.

Oxygen, thermal conductivity, Refs. 21, 30, 38, 43, 45, 49-56

temperature range 75 - 1173°K.

5. VISCOSITY

As in the method described for argon, the suitabilities of the potential functions above were investigated by first observing the variation of ϵ/k with T at a fixed R , then observing any subsequent changes caused by varying R . Accordingly, for a particular function, experimental values of η and the corresponding temperatures were substituted in Eq (5) together with a sensible value for R , hence obtaining $\Omega^{(2,2)*}$ as a function of T . An interpolation computer routine then generated T^* by inserting the calculated $\Omega^{(2,2)*}$ into a given set of $\Omega^{(2,2)*}(T^*)$ for the function. From T^* and the expression $\epsilon/k = T/T^*$, ϵ/k was then computed as a function of T . This procedure was repeated for several values of R , varying R by about 10% overall. The same experimental data were used for all four potential functions.

The best value of R was that value associated with the curve that had the least variation of ϵ/k over the widest temperature range allowing for the approximate 1% experimental and interpolation error. We thus estimated ϵ/k to about 1% and R to about 0.2%.

5.1 NITROGEN

For the Lennard-Jones potential the best value of σ was selected at $\sigma = 3.68 \text{ \AA}$. Figure 1 shows the best value and also two other curves which show the patterns caused by an approximately 5% change in σ . Note the pattern is the same as found for argon. A best value of ϵ/k from Fig. 1 is seen to be about 90°K, and this was adjusted to

$\epsilon/k = 90.9^\circ\text{K}$ (Table I) to obtain agreement between the experimental and calculated viscosity coefficients at 293°K . The reason for choosing 293°K is because the viscosity coefficient at that temperature has been carefully measured by several workers [e.g., Refs. 13, 14, 17] with close agreement. Figure 5 shows a percentage deviation curve for the Lennard-Jones potential using the selected σ and ϵ/k . It was verified that the choice of a given set of collision integrals did not alter the conclusions or the best values of σ or ϵ/k by any significant amount.

TABLE I

Best values of the parameters obtained from each potential function for nitrogen.

Function	ϵ/k , $^\circ\text{K}$	R , \AA
L - J	90.9	3.68
Kihara ($\gamma = 0.2$)	116.7	3.55
Exp: 6 ($\alpha = 17.0$)	104.3	3.99
Morse ($c = 5.0$)	74.8	3.82

The best values of the Kihara potential function were found for five values of the parameter γ . The best value graphs of ϵ/k - vs - T for each value of γ are shown in Fig. 2, and it was decided that the most suitable of these was $\gamma = 0.2$, $\sigma = 3.55 \text{ \AA}$. Again, obtaining agreement between the experimental and calculated viscosity coefficient at 293°K , the value of ϵ/k chosen was $\epsilon/k = 116.7^\circ\text{K}$ (Table I) and the deviation curve (Fig. 6) was plotted.

The Exp: 6 was treated in the same manner and the best value plot for the different values of α are shown in Fig. 3. Here $\alpha = 17$ was chosen with $r_m = 3.99 \text{ \AA}$ (Table I) and $\epsilon/k = 104.3^\circ\text{K}$. The deviation curve is shown in Fig. 5.

It is remarked that the behavior of the variation of R is very similar for these functions as was found for argon.

The Morse function, treated in the same fashion, has the best value σ curves shown for $c = 4, 5$, and 6 (Fig. 4). Here $c = 5$ was chosen with $\sigma = 3.82 \text{ \AA}$ and $\epsilon/k = 74.8^\circ\text{K}$. Figure 4 also shows the variation of σ at $c = 5$. It is evident, by comparing the Morse deviation curve (Fig. 5) with those of the other functions for nitrogen, that the Morse is the least satisfactory of the four.

5.2 OXYGEN

Oxygen was treated by exactly the same procedure as described for nitrogen. The pattern of the curves as R was varied for a given α , γ , or c was the same, and we list in Table II the best values of R and the corresponding best values of ϵ/k for all functions. The percentage deviation curves (Fig. 7) compare the functions. The Kihara function, $\gamma = 0.1$, again was chosen as the best function (Fig. 6), while the Morse function was again the least satisfactory.

TABLE II

Best values of the parameters obtained from each potential function for oxygen.

Function	$\epsilon/k, ^\circ\text{K}$	$R, \text{\AA}$
L - J	110.7	3.44
Kihara ($\gamma = 0.1$)	124.5	3.38
Exp: 6 ($\alpha = 16.0$)	121.6	3.78
Morse ($c = 5.0$)	98.7	3.53

SUMMARY: For nitrogen, the chosen best function with parameters was the Kihara, $\gamma = 0.2$, $\epsilon/k = 116.7^\circ\text{K}$, $\sigma = 3.55 \text{ \AA}$. Similarly, for oxygen, Kihara, $\gamma = 0.1$, $\epsilon/k = 124.5^\circ\text{K}$, $\sigma = 3.38 \text{ \AA}$.

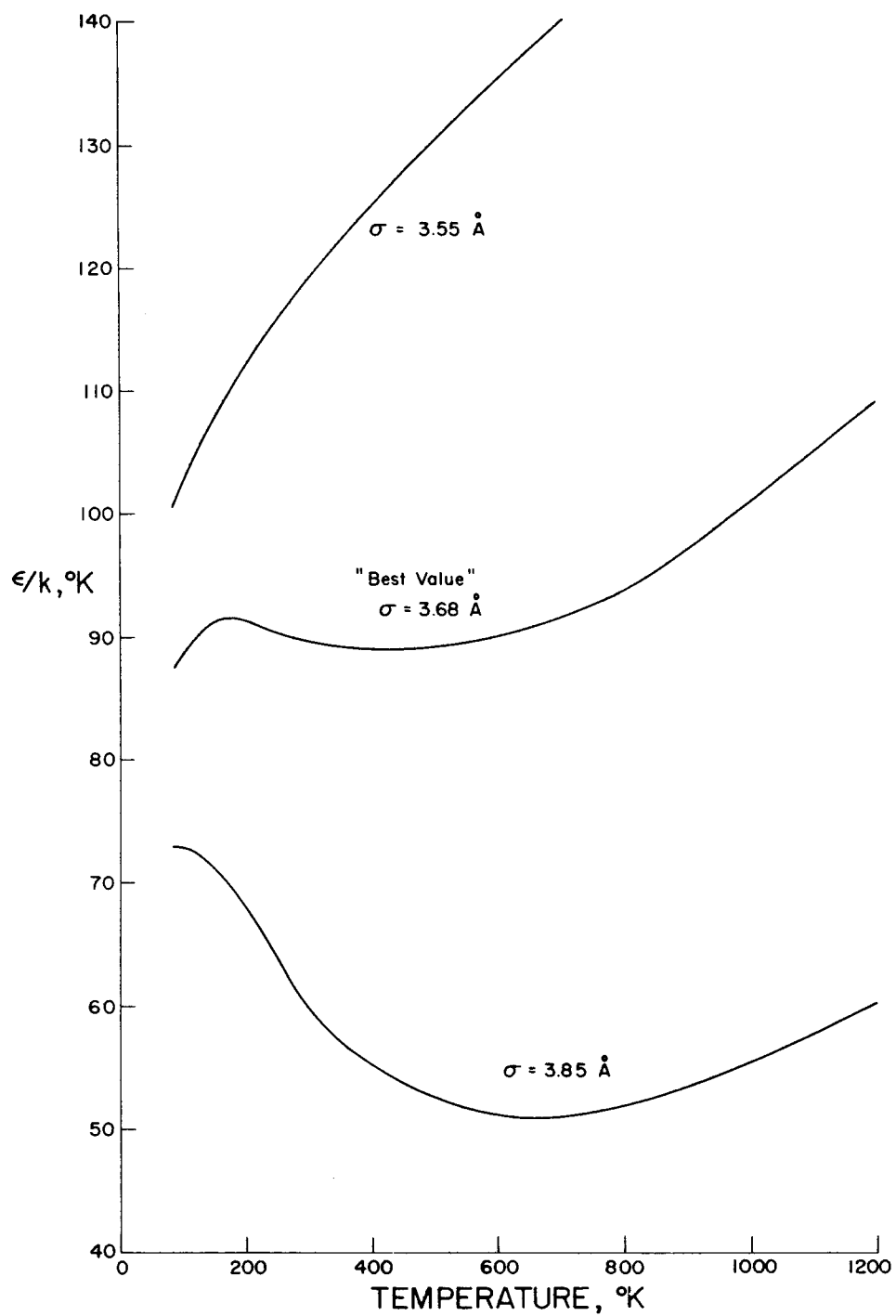


Fig. 1. Variation of ϵ/k versus T (both in degrees Kelvin) for selected values of σ using the Lennard-Jones potential function for nitrogen.

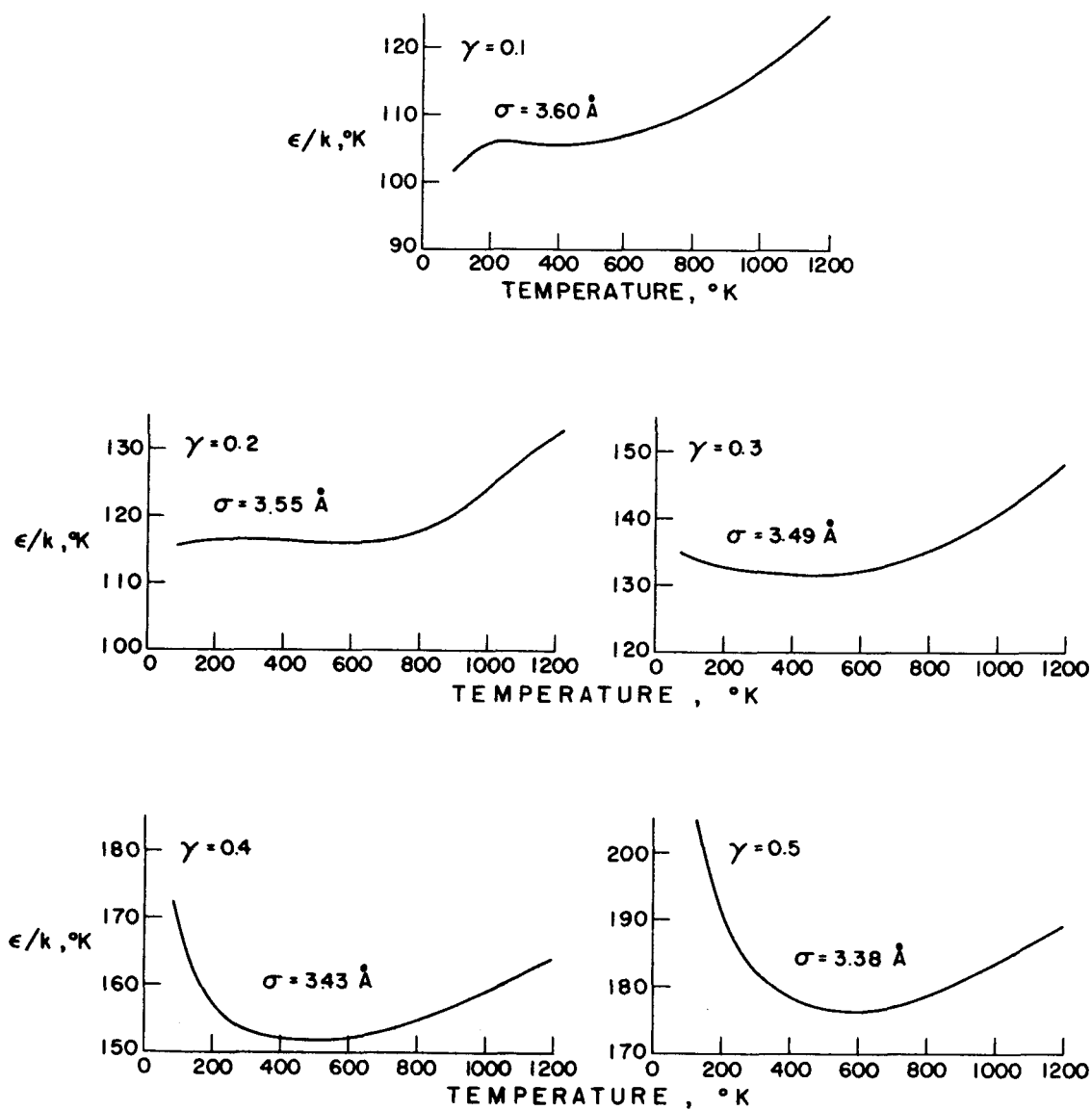


Fig. 2. Best values of σ for various values of γ for the Kihara potential function for nitrogen.

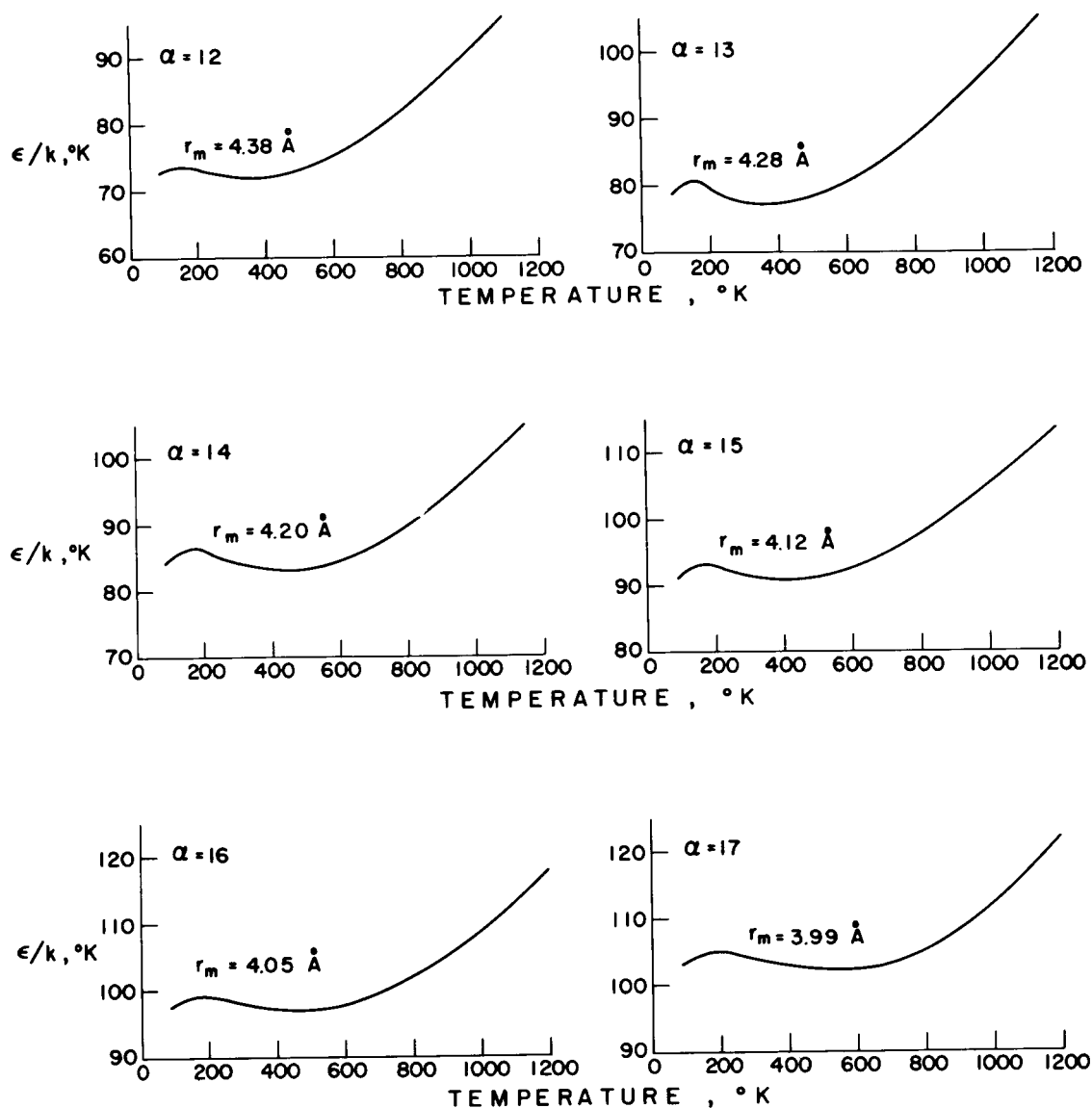
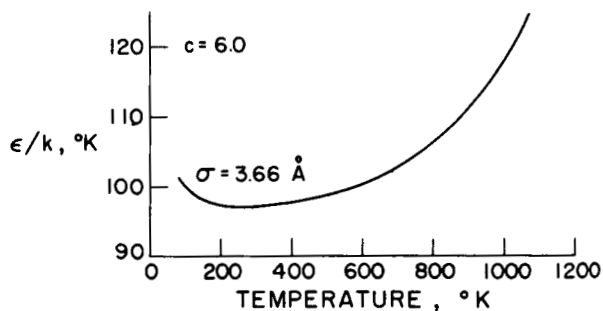
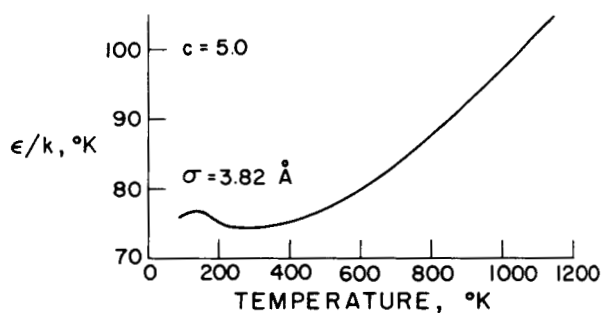
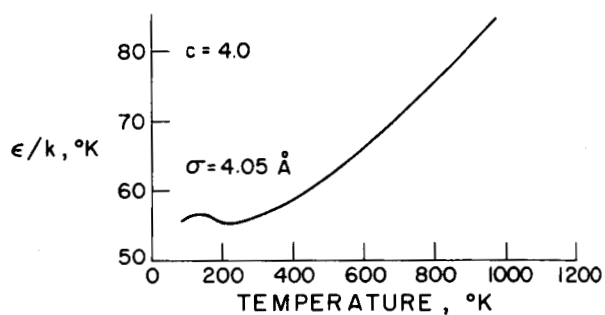
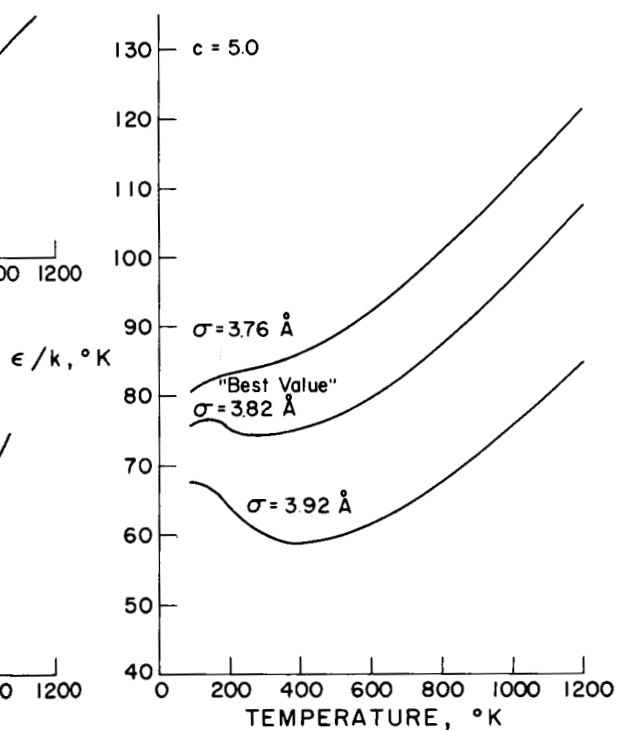


Fig. 3. Best values of r_m for various values of α for the Exp: 6 potential function for nitrogen.



(a)



(b)

Fig. 4. (a) Best values of σ for three values of c for the Morse potential function. (b) Variation of σ for a given value of c . Nitrogen.

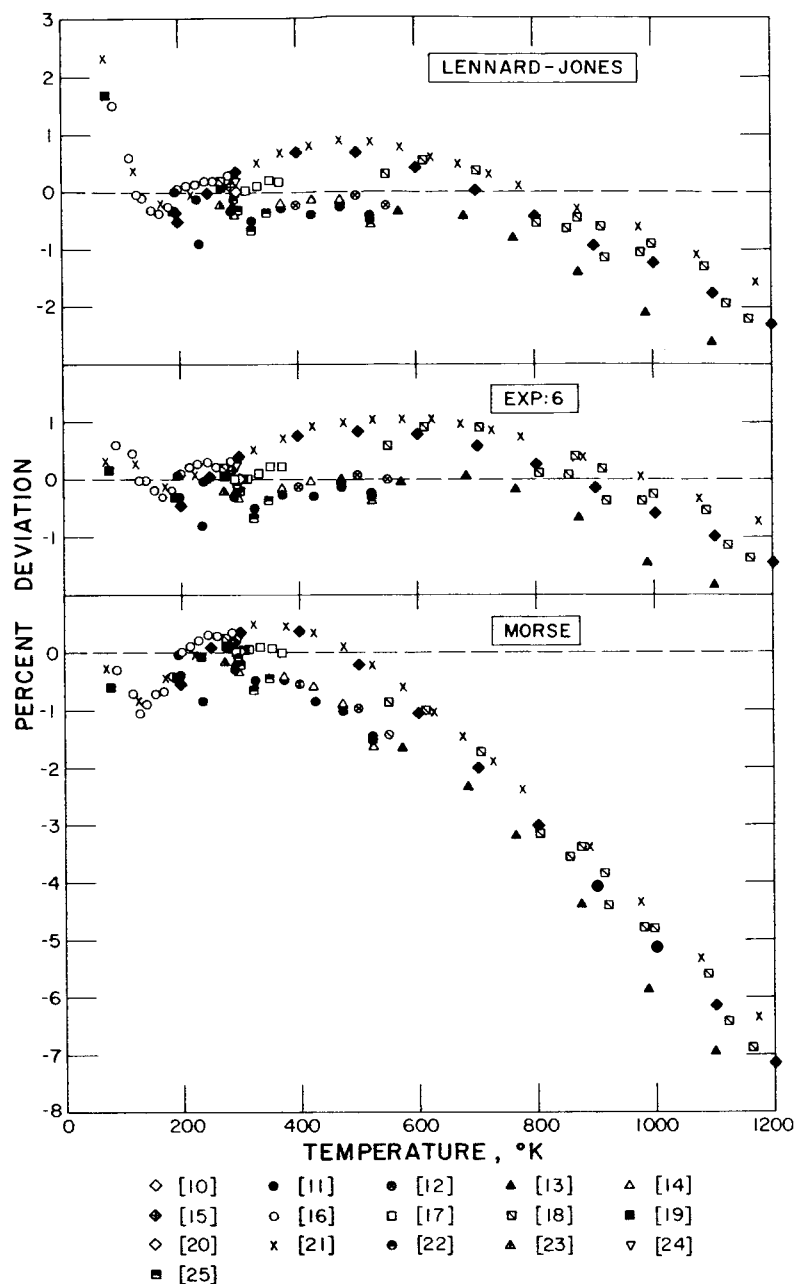


Fig. 5. Nitrogen percent deviation curves $\left[\left(\frac{\eta_{exp} - \eta_{calc}}{\eta_{calc}} \right) \times 100 \right]$ of experimental and calculated viscosity coefficients for three potential functions using the best values selected by the method explained in the text.

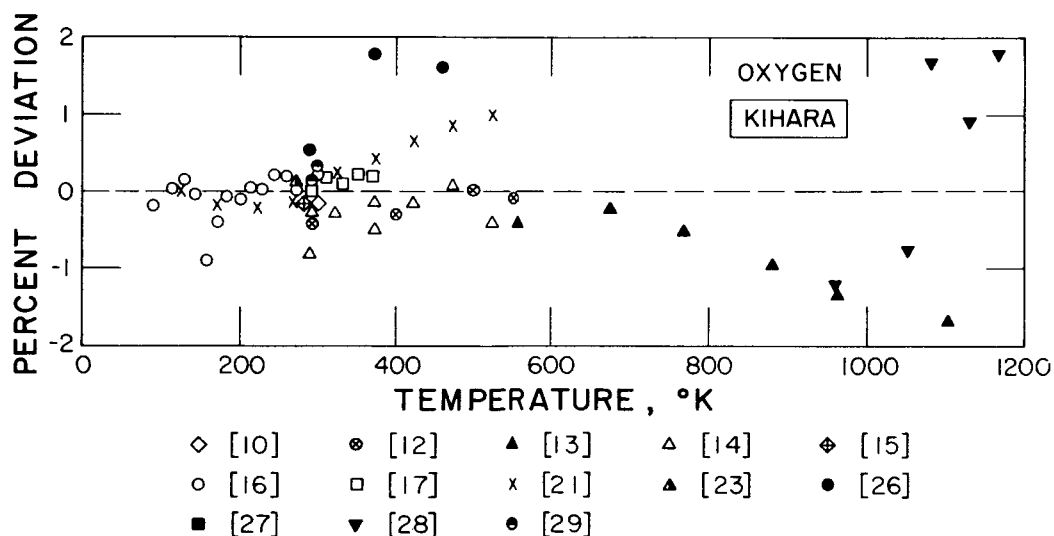
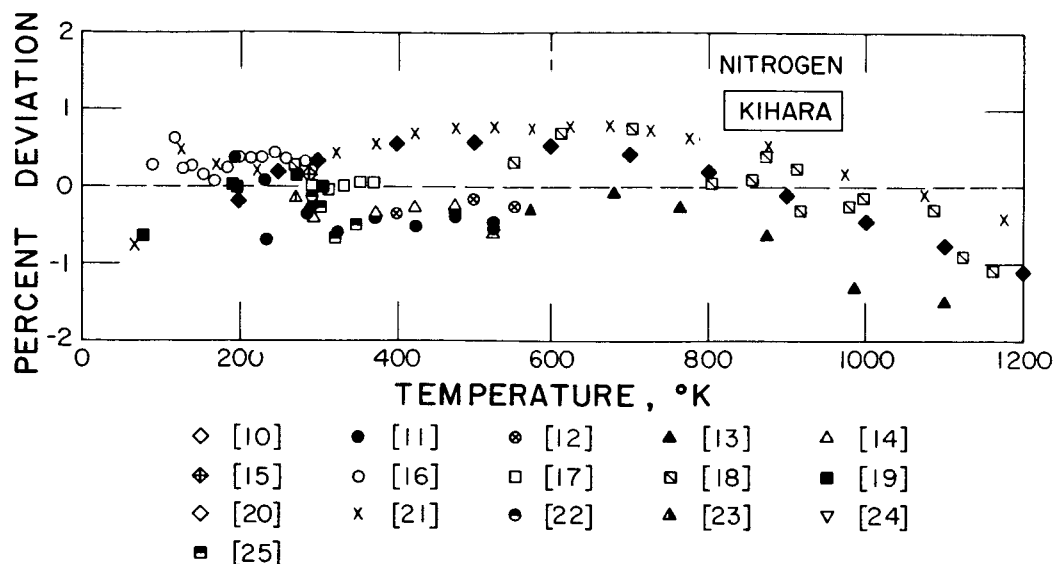


Fig. 6. Nitrogen and oxygen deviation curves calculated from the Kihara functions (for nitrogen $\gamma = 0.2$, for oxygen $\gamma = 0.1$). These functions were selected as the best. Note: the high temperature values of viscosity from Ref. 28 are known to be in error (private communication - C. J. G. Raw).

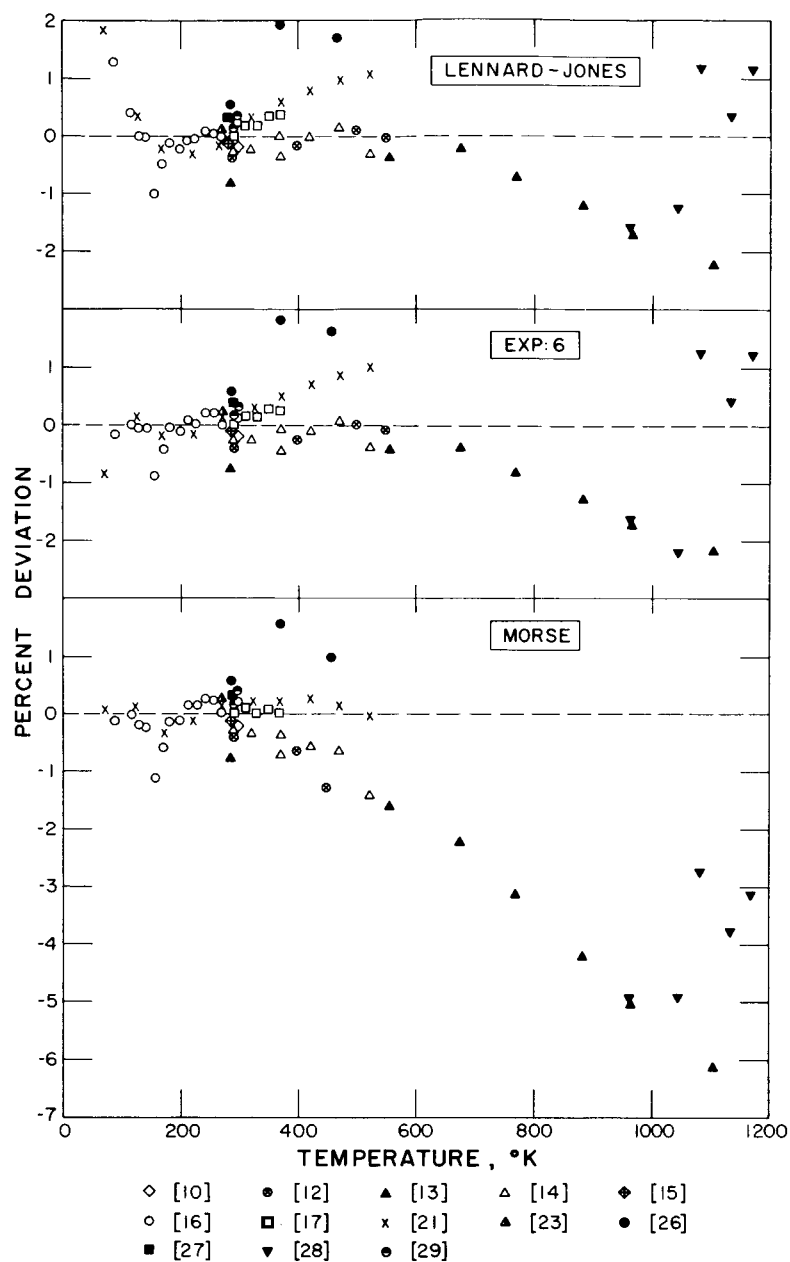


Fig. 7. Oxygen percent deviation curves for three functions.
 Note: in Figs. 5-7 some experimental points were omitted in the temperature range 273-300°K for clarity of presentation. The experimental values omitted were from Refs. 11, 12, 14, 16, 20, 21 for nitrogen and Refs. 14, 16 for oxygen.

6. THERMAL CONDUCTIVITY

The coefficient λ_{dilute} was calculated from Eq (6) with the best function and best values of the function for nitrogen and oxygen respectively. The Eucken correction to λ_{dilute} (Eq (7)) was then added with specific heats taken from Ref. 57. Percentage deviation curves (Fig. 8) were plotted for both gases. It is seen that the experimental data deviates systematically from the theoretical predictions of Eq (7), although agreement is reasonable in the limited temperature range 200-300 °K. The Eucken correction has usually been tested in this limited region. It is easily verified that any realistic errors in C_v would not produce this pattern and that, hence, despite the large scatter in the data, the Eucken correction is not satisfactory. This correction will be examined in more detail in a later publication.

Rather than further empirically modify the equation for λ , it was decided to represent the thermal conductivity coefficients by a polynomial in the temperature. Selected data [nitrogen, Refs. 30, 36, 37, 39, 40, 44, 45; oxygen, Refs. 30, 45, 52, 53, 56] were fitted by the method of least squares and the equations below were most suitable.

Nitrogen

$$\lambda 10^6 = -16.20 + 1.28825 T - 1.65770 (10^{-3}) T^2 + 1.66105 (10^{-6}) T^3 - 6.1505 (10^{-10}) T^4 \quad (8)$$

Oxygen

$$\lambda 10^6 = -14.24 + 1.11127 T - 6.7362 (10^{-4}) T^2 + 2.9405 (10^{-7}) T^3, \quad (9)$$

where: λ = the thermal conductivity of the gas.

T = the absolute temperature, °K.

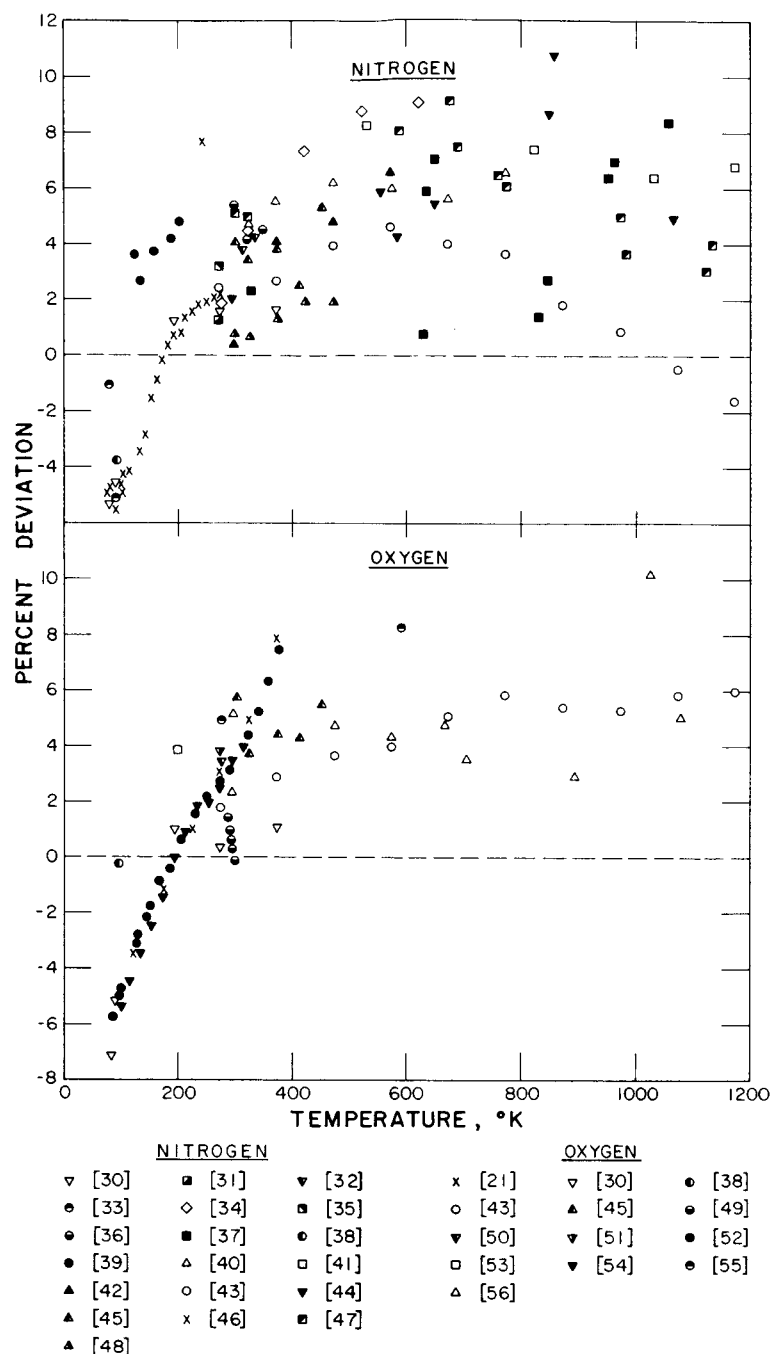


Fig. 8. Percent deviation curves $\left[\left(\frac{\lambda_{exp} - \lambda_{calc}}{\lambda_{calc}} \right) \times 100 \right]$

for the thermal conductivity of nitrogen and oxygen. λ_{calc} was calculated from Eq (7) which included the Eucken correction using the Kihara function with parameters given in Tables I and II.

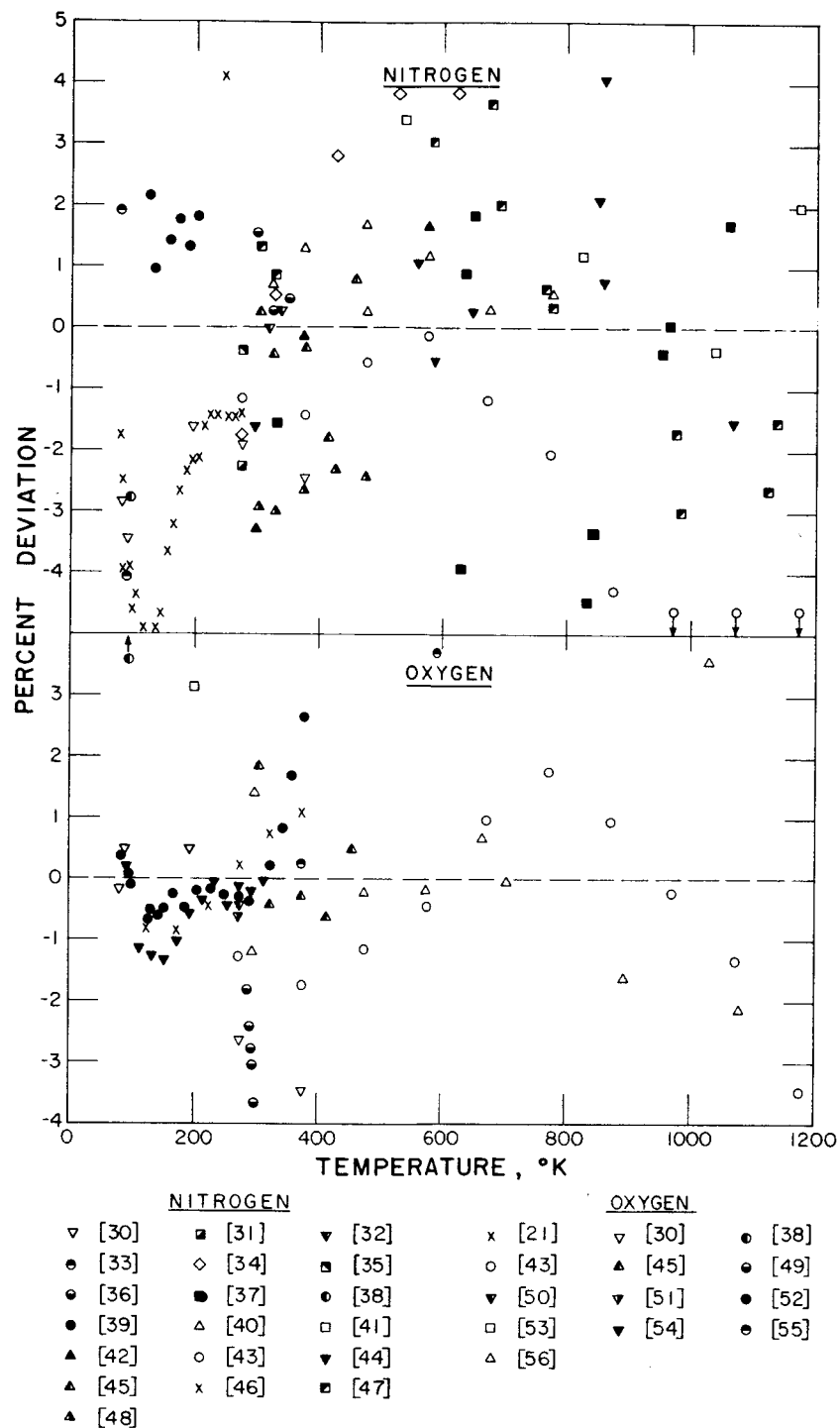


Fig. 9 Percent deviation curves of selected experimental thermal conductivity data calculated from Eqs (8) and (9).

The data were not suitable to justify a rigorous approach to the least squares fit, although this would have been the best procedure. As the experimental inaccuracy precluded sensible weighting of the data, the data were unweighted. The deviation curves (Fig. 9) were plotted.

7. CONCLUSION

It has been shown that the kinetic theory expression for viscosity is suitable to correlate data using the functions and parameters given in Section 5. It does not, however, appear possible to apply kinetic theory to the thermal conductivity coefficient at present. The usual thermal conductivity expression for a polyatomic gas, i.e., the kinetic theory equation plus the Eucken correction, was found unsuitable for nitrogen and oxygen. It is noted that more involved formulization of the Eucken corrections are known; for example, Chapman and Cowling [58] write

$$\lambda = \left\{ \frac{15}{4} (\gamma - 1) + \frac{1}{2} u_{11} (5 - 3\gamma) \right\} \eta_{\text{dilute}} C_v, \quad (10)$$

where γ is the ratio of the specific heats and u_{11} a factor which has a value of about 1.2. A comparison of Eq (10) with experiment would reduce the high temperature deviations (Fig. 8) but would increase the deviations at low temperature. As u_{11} also would have to be found from experiment, it was felt that fitting the data by a polynomial equation is as suitable as applying Eq (10) or another similar correction. As stated above, the Eucken correction will be studied further.

There is another problem with the correlation of thermal conductivity: not only are the data widely scattered, but it is not always known if the scatter is about "true" mean values. It is highly probable

that the experimental results also exhibit systematic error. (Systematic error can, of course, affect viscosity measurements but not to such an extent.) The polynomial fits cannot take such errors into account.

Tables in the temperature range 100 - 1000 °K have been computed and are given in Tables III and IV for nitrogen and oxygen respectively. The viscosity tables are estimated to be accurate to 2% and the thermal conductivity tables accurate to 5%.

8. ACKNOWLEDGMENT

This work was supported by a grant from NASA, Contract Number R-06-006-046.

TABLE III. VISCOSITY AND THERMAL CONDUCTIVITY
OF GASEOUS NITROGEN*

TEMPERATURE	VISCOSITY	THERMAL CONDUCTIVITY	TEMPERATURE	VISCOSITY	THERMAL CONDUCTIVITY
K	G/CM-SEC $\eta 10^6$	J/CM-SEC-DEG $\lambda 10^6$	K	G/CM-SEC $\eta 10^6$	J/CM-SEC-DEG $\lambda 10^6$
			500	256.4	382.7
			510	259.8	388.4
			520	263.3	394.0
			530	266.6	399.7
			540	270.0	405.3
			550	273.3	411.0
			560	276.6	416.6
			570	279.9	422.2
			580	283.1	427.8
			590	286.4	433.4
100	69.3	97.6	600	289.5	439.1
110	75.8	107.6	610	292.7	444.7
120	82.2	117.3	620	295.8	450.3
130	88.5	126.7	630	299.0	455.9
140	94.7	136.0	640	302.1	461.5
150	100.7	145.0	650	305.0	467.2
160	106.7	153.9	660	308.1	472.8
170	112.4	162.5	670	311.1	478.4
180	118.1	171.0	680	314.1	484.1
190	123.7	179.3	690	317.1	489.7
200	129.2	187.4	700	320.0	495.4
210	134.5	195.4	710	323.0	501.0
220	139.8	203.2	720	325.9	506.7
230	144.9	210.9	730	328.8	512.3
240	149.9	218.4	740	331.7	518.0
250	154.8	225.8	750	334.6	523.7
260	159.7	233.1	760	337.5	529.3
270	164.4	240.2	770	340.3	535.0
280	169.1	247.2	780	343.2	540.7
290	173.7	254.1	790	346.0	546.3
300	178.2	260.9	800	348.8	552.0
310	182.7	267.7	810	351.6	557.7
320	187.1	274.3	820	354.4	563.3
330	191.4	280.8	830	357.1	568.9
340	195.6	287.2	840	359.8	574.6
350	199.8	293.6	850	362.6	580.2
360	203.9	299.9	860	365.3	585.7
370	207.9	306.1	870	367.9	591.3
380	211.9	312.3	880	370.6	596.9
390	215.8	318.4	890	373.3	602.4
400	219.7	324.4	900	375.9	607.9
410	223.6	330.4	910	378.5	613.3
420	227.4	336.4	920	381.2	618.7
430	231.2	342.3	930	383.8	624.1
440	234.9	348.1	940	386.4	629.5
450	238.6	354.0	950	389.0	634.7
460	242.2	359.8	960	391.6	640.0
470	245.8	365.5	970	394.2	645.2
480	249.4	371.3	980	396.7	650.3
490	252.9	377.0	990	399.3	655.4
			1000	401.7	660.4

*Viscosities calculated for the dilute gas by Kihara potential, with $\gamma = 0.2$, $\sigma = 3.55 \text{ \AA}$, $\epsilon/k = 116.7^\circ\text{K}$. Thermal conductivities from Eq (8).

TABLE IV. VISCOSITY AND THERMAL CONDUCTIVITY
OF GASEOUS OXYGEN*

TEMPERATURE	VISCOSITY	THERMAL CONDUCTIVITY	TEMPERATURE	VISCOSITY	THERMAL CONDUCTIVITY
K	G/CM-SEC $\eta 10^6$	J/CM-SEC-DEG $\lambda 10^6$	K	G/CM-SEC $\eta 10^6$	J/CM-SEC-DEG $\lambda 10^6$
			500	301.6	409.7
			510	305.8	416.3
			520	310.0	422.8
			530	314.1	429.3
			540	318.2	435.7
			550	322.2	442.1
			560	326.2	448.5
			570	330.2	454.8
			580	334.2	461.1
			590	338.0	467.3
100	76.7	90.4	600	341.9	473.5
110	84.2	100.2	610	345.8	479.7
120	91.7	109.9	620	349.6	485.9
130	99.1	119.5	630	353.4	492.0
140	106.4	128.9	640	357.2	498.1
150	113.5	138.3	650	360.9	504.2
160	120.6	147.5	660	364.7	510.3
170	127.6	156.7	670	368.3	516.4
180	134.4	165.7	680	372.0	522.4
190	141.0	174.6	690	375.6	528.4
200	147.5	183.4	700	379.2	534.4
210	154.0	192.1	710	382.8	540.4
220	160.3	200.8	720	386.3	546.4
230	166.5	209.3	730	389.8	552.4
240	172.6	217.7	740	393.3	558.4
250	178.5	226.1	750	396.8	564.4
260	184.3	234.3	760	400.3	570.3
270	190.1	242.5	770	403.8	576.3
280	195.8	250.6	780	407.2	582.3
290	201.3	258.5	790	410.7	588.2
300	206.7	266.5	800	414.1	594.2
310	212.1	274.3	810	417.5	600.2
320	217.4	282.0	820	420.9	606.2
330	222.6	289.7	830	424.3	612.2
340	227.7	297.3	840	427.6	618.2
350	232.9	304.8	850	431.0	624.2
360	237.9	312.2	860	434.3	630.3
370	242.8	319.6	870	437.7	636.3
380	247.7	326.9	880	441.0	642.4
390	252.5	334.1	890	444.2	648.5
400	257.2	341.3	900	447.3	654.6
410	261.9	348.4	910	450.6	660.8
420	266.5	355.5	920	453.8	666.9
430	271.1	362.4	930	457.0	673.1
440	275.6	369.4	940	460.2	679.4
450	280.0	376.2	950	463.4	685.6
460	284.4	383.0	960	466.5	691.9
470	288.8	389.8	970	469.6	698.3
480	293.1	396.5	980	472.8	704.6
490	297.3	403.1	990	475.9	711.0
			1000	478.6	717.5

*Viscosities calculated for the dilute gas by the Kihara potential, with $\gamma = 0.1$, $\sigma = 3.38 \text{ \AA}$, $\epsilon/k = 124.5^\circ\text{K}$. Thermal conductivities from Eq (9).

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